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N, then the axes of one set of translationally equivalent molecules have the direction cosines in the **a**, **b**, **c** (crystal) system of axes

$$L_1=\begin{pmatrix}-0.435\\-0.223\\+0.875\end{pmatrix},\quad M_1=\begin{pmatrix}-0.322\\-0.870\\-0.371\end{pmatrix},\quad N_1=\begin{pmatrix}+0.840\\-0.443\\+0.331\end{pmatrix}.$$

The second set of translationally equivalent molecules may be found by reflection in a plane perpendicular to the b axis of the crystal:

$$L_2=\begin{pmatrix}-0.435\\+0.223\\+0.875\end{pmatrix},\quad M_2=\begin{pmatrix}-0.322\\+0.870\\-0.371\end{pmatrix},\quad N_2=\begin{pmatrix}+0.840\\+0.443\\+0.331\end{pmatrix}.$$

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Closed Form of Infinite Series Used in Some Atomic Integrals Containing r_{12}, r_{13}, and r_{23}

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In an excellent scheme recently developed for evaluating the integral

$$\int f_1(r_1)f_2(r_2)f_3(r_3)g_1(r_{12})g_2(r_{23})g_3(r_{13})\,(dv)$$

met in the calculation of correlated atomic wavefunctions, certain functions required in the computational scheme had to be evaluated by an infinite series expansion. As many as 40 terms may be needed in each of the three required infinite summations to get eight significant figures. We give a closed form expression for such functions avoiding all infinite sums. The new result is very compact and avoids the previous difficulty of numerical stability.

INTRODUCTION

AN excellent scheme for evaluating certain atomic integrals that have an explicit dependence on three interelectronic coordinates, e.g., r_{12}, r_{13}, and r_{23}, in the integrand has been described by Öhrn and Nordling.[1] This is the most difficult integral in the calculation of correlated atomic wavefunctions for it contains the three interelectronic coordinates in a nonseparable way:

$$\int f_1(\mathbf{r}_1)f_2(\mathbf{r}_2)f_3(\mathbf{r}_3)g_1(r_{12})g_2(r_{23})g_3(r_{13})\,(dv). \quad (1)$$

This integral is expressed[1] as a rapidly convergent infinite series of other integrals. With the radial parts of the functions $f_i(\mathbf{r}_i)$ restricted to Slater-type orbitals and $g(r_{ij})$ to powers of the interelectronic distance, these latter integrals are expressed in terms of auxiliary functions V and W.[1] For certain arguments of these auxiliary functions their computational scheme includes three infinite sums requiring as many as 40 to 60 terms each to get eight significant figures in the answer. We remove this difficulty by giving a closed-form expression for such terms. This avoids problems of numerical stability. With a very special choice of the arguments of our functions we have found a known expression for a special case of a hypergeometric function that comes up in the study of multiple correlation coefficients in statistics.[2] Our results agree with available tabulations throughout.

THEORY AND RESULTS

To put our results in context we first need some of Öhrn and Nordling's results. The simplest nontrivial type of integral [Eq. (1)] can be written, after decomposition of products of spherical harmonics, as a finite sum of integrals, $I_{hij}{}^{tuv}$

$$I_{hij}{}^{tuv}=(4\pi)^{-\frac{1}{2}}\int f_1(r_1)f_2(r_2)f_3(r_3)\,Y_h{}^t(1)\,Y_j{}^v(2)\,Y_i{}^u(3)\times g_1(r_{12})g_2(r_{23})g_3(r_{13})\,(dv). \quad (2)$$

* Contribution No. 3202.

[1] Y. Öhrn and J. Nordling, J. Chem. Phys. **39**, 1864 (1963).

[2] Editorial appendix to a paper by J. Wishart, Biometrika **22**, 362 (1930).

The functions $f_i(r)$ are the radial parts of the orbital form of $f_i(\mathbf{r}_i)$ and the spherical harmonics result from the decomposition of the angular dependence of these orbitals. The integrals $I_{hij}{}^{tuv}$ then become

$$I_{hij}{}^{tuv}=\sum_{k,l,m} B_{klm}(ht \mid iu \mid jv)\, U_{klm}(g_1, g_3, g_2). \quad (3)$$

B_{klm} and U_{klm} come from the angular and radial integrations respectively and k, l, and m are, in principle, infinite. In the example of their computational scheme[1] they take $f_1(x)=e^{-\alpha x}x^p$, $f_2(y)=e^{-\beta y}y^q$, $f_3(z)=e^{-\gamma z}z^s$, and $g_1(r_{ij})=r_{ij}{}^\lambda$ and the integral $I_{hij}{}^{tuv}$ becomes parametrically $I(\alpha, \beta, \gamma \mid p, q, s \mid \lambda, \mu, \nu)$. The integral is now expressed in terms of the auxiliary function W:

$$W(\alpha, \beta, \gamma \mid f, g, h)=\int_0^\infty e^{-\alpha x}x^f dx \int_x^\infty e^{-\beta y}y^g dy \int_y^\infty e^{-\gamma z}z^h dz. \quad (4)$$

The recurrence relation for W uses another auxiliary function V

$$V(\alpha, \beta \mid m, n)=\int_0^\infty e^{-\alpha x}x^m dx \int_x^\infty e^{-\beta y}y^n dy. \quad (5)$$

For $h\geq 0$ all W functions are easily evaluated but for $h<0$ they were forced to an infinite series expansion for their computational scheme. This infinite series actually contains three infinite sums, and they write for $h<0$:

$$W(\alpha, \beta, \gamma \mid f, g, h)=W_0\{X_0\sum_{\mu=1}^{M}x_\mu+\sum_{\mu=2}^{M}y_\mu\}. \quad (6)$$

M is infinite and X_0 involves another infinite sum.[1] W_0, x_μ, and y_μ are simple expressions.[1] For example, in $W(4, 1, 1 \mid 0, 0, -1)$, representative of the worst convergence properties possible, M and N must be 60 and 40, respectively, to get eight significant figures. By the method we now give this integral is simply

$$W(4, 1, 1 \mid 0, 0, -1)=\tfrac{1}{8}\log 6-\tfrac{1}{4}\log 3 \quad (7)$$

We first obtain a closed-form expression for $V(\alpha, \beta \mid m, -1)$ and then with this a simple expression for $W(\alpha, \beta, \gamma \mid f, g, -1)$. Generalizations to h or n [Eqs. (4) and (5)] <-1 are obvious through the recurrence relation between $V(\alpha, \beta \mid m, -n)$ and $V(\alpha, \beta \mid m, -n+1)$, e.g., $n\geq 2$ and $m\geq n+1$ (see Ref. 1). The exponential integral $E_1(x)$ is

$$E_1(x)=\int_x^\infty e^{-t}t^{-1}dt, \quad (8)$$

and then

$$V(\alpha, \beta \mid m, -1)=\beta^{-m-1}\int_0^\infty e^{-st}t^m E_1(t)\,dt \quad (9)$$

with $s=\alpha/\beta$. Either by direct expansion of the integrand or from the Bateman Manuscript Project[3] we write for $m>-1$

$$\int_0^\infty e^{-st}t^m E_1(t)\,dt = m!(m+1)^{-1}(1+s)^{-m-1}F[1, m+1; m+2; s/(1+s)], \quad (10)$$

where F is the hypergeometric function

$$F(a, b; c; z)=\sum_{n=0}^{\infty}[(a)_n(b)_n/(c)_n n!]z^n \quad (11)$$

and $(a)_n=\Gamma(a+n)/\Gamma(a)$ with $\Gamma(a)$ the usual gamma function. The equation (10) is still an infinite series, and for the arguments on its hypergeometric function we have:

$$F(1, m+1; m+2; \theta)=(m+1)\sum_{n=0}^{\infty}\frac{\theta^n}{(m+n+1)}. \quad (12)$$

But the infinite sum in Eq. (12) can be summed by integration and the integral evaluated in closed form. Observe that

$$\sum_{n=0}^{\infty}\frac{\theta^n}{(m+n+1)}=\sum_{n=0}^{\infty}\int_0^\infty \exp[-(m+1)t](\theta e^{-t})^n dt, \quad (13)$$

and therefore

$$F(1, m+1; m+2; \theta)=(m+1)\int_0^\infty \frac{\exp[-(m+1)t]}{1-\theta e^{-t}}dt. \quad (14)$$

The integral in Eq. (14) is easily evaluated. With some more algebra we get

$$V(\alpha, \beta \mid m, -1)=-m!\alpha^{-m-1}[\log(1-\theta)+\sum_{n=1}^{m}(\theta^n/n)], \quad (15)$$

with $\theta=\alpha(\alpha+\beta)^{-1}$. We now express $W(\alpha, \beta, \gamma \mid f, g, -1)$ in terms of $V(\alpha, \beta \mid m, -1)$ for $g\geq 0$:

$$W(\alpha, \beta, \gamma \mid f, g, -1) = \sum_{k=0}^{g}\frac{g!}{(g-k)!}\beta^{-k-1}V(\alpha+\beta, \gamma \mid f+g-k, -1) - g!\beta^{-g-1}V(\alpha, \beta+\gamma \mid f, -1) - \sum_{k=0}^{g-1}\frac{g!}{(g-k)!}\beta^{-k-1}V(\alpha, \beta+\gamma \mid f, g-k-1). \quad (16)$$

Equation (15) is used to evaluate all the V's in Eq. (16) with $n=-1$ [Eq. (5)]. We then have a closed form expression for $W(\alpha, \beta, \gamma \mid f, g, -1)$ which avoids the infinite sums used in Ref. 1 and has good numerical stability.

NUMERICAL RESULTS

This section gives actual results using these equations. In their numerical results Öhrn and Nordling[1] evaluated $I_{000}{}^{000}$ [Eq. (8)] writing

$$I(\alpha, \beta, \gamma \mid p, q, s \mid 1, 1, -1)=\sum_{k=0}^{\infty}D_k. \quad (17)$$

[3] See Bateman Manuscript Project, *Higher Transcendental Functions*, edited by A. Erdelyi (McGraw-Hill Book Company, Inc., New York, 1953), Vol. 2, p. 144.

See Ref. 1 for the exact expressions for the D_k's. The first term that contains W functions with negative h [Eq. (4)] is D_1. Terms with higher k contain many of them too. D_1 is about 1.5% of D_0 and is listed[1] as $D_1=0.0049134950\times10^{-5}$ with $M=N=40$ and double-precision arithmetic. Using our Eq. (16) for the W's with $h=-1$, we find $D_1=0.0049135\times10^{-5}$ without double-precision arithmetic. For this particular I [Eq. (17)], convergence is rapid, e.g., $D_1/D_0=1.5\%$, but for other I's with k, l, m not all zero, convergence is slower and the second term may be 8% of the first.[4] Higher terms in the series will involve more W's with $h\leq-1$. This is then a direct numerical test of our results. No infinite series of any type is involved. In the previous section we wrote as another example of the use of our results Eq. (7)

$$W(4,\,1,\,1\,|\,0,\,0,\,-1)=\tfrac{1}{5}\log6-\tfrac{1}{4}\log3=0.083698822. \tag{18}$$

Although there is no numerical value listed for this integral in Ref. 1, from their Table I they needed $M=60$, $N=40$ to get this to eight significant figures.

From Eq. (14) we also get

$$F(1,\,1;\,2,\,\theta)=-\theta^{-1}\log(1-\theta). \tag{19}$$

[4] V. McKoy and O. Sinanoğlu, J. Chem. Phys. **41**, 2689 (1964).

As a further check on our results we use Eq. (19) to get $F(1,\,1,\,2,\,\theta)$ and compare it with some values of this function tabulated in Ref. 2. The hypergeometric function $F[1,\,1,\,\frac{1}{2}(m+1),\,\theta]$ comes up in the study of multiple correlation coefficients in statistics.[5] For $n=3$ this becomes $F(1,\,1,\,2,\,\theta)$. For example at $\theta=0.16$ and 0.25, $F(1,\,1,\,2,\,\theta)$ are 1.089709 and 1.150728 from Eq. (19). These differ from the values listed in Ref. 2 only by 1 or 2 in the last significant figure.

CONCLUSION

Öhrn and Nordling[1] have expressed the most difficult integral in the calculation of correlated atomic wavefunctions [Eq. (1)] in an infinite series of other integrals [see Eq. (3)]. Their scheme is the best yet proposed. However, in their computational scheme they needed another infinite series expansion. We have shown that this second infinite series expansion can indeed be summed and the results are in a very compact form useful for machine computations. This result will be even more useful in correlation-energy calculations on electrons other than s electrons.[4]

[5] $F(2,\,2,\,3,\,\theta)$ is also used. This can also be evaluated as in Eq. (12) by noting

$$(1-x)^{-2}=\sum_{n=0}^{\infty}(n+1)x^n.$$

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Vibrational Relaxation in Liquid Dichloromethane*

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Measurements of ultrasonic absorption have been conducted in liquid dichloromethane over a frequency range of 30 to 510 Mc/sec, and over a temperature range of −60° to 25°C. The relaxation is exceedingly strong. The experimental values are predictable by the assumption that the vibrational specific heat of the molecule is the chief cause of the absorption, if it is assumed that the first vibrational mode is inactive, as hypothesized by Andreae. The frequencies of relaxation, arrived at through a curve of best fit, are 171 Mc/sec at 25°C, 147 Mc/sec at 0°C, and 117 Mc/sec at −60°C. The measured velocity dispersion is in agreement with the magnitude of the relaxing specific heat of vibration.

INTRODUCTION

ULTRASONIC absorption measurements in liquid dichloromethane have been conducted by Andreae[1] and by Andreae, Joyce, and Oliver,[2] who have found a strong relaxation effect with the relaxation frequency at 170 Mc/sec. They have interpreted the effect as a partial relaxation of the vibrational specific heat of the molecule, computing the specific heat from infrared and Raman spectra. Their results in the liquid agree with the dispersion measurements of Sette, Busala, and Hubbard[3] in dichloromethane gas, in which a multiple-relaxation effect was found. These authors interpreted the cause of the measured relaxation as the higher-frequency vibrational modes of the molecule, and hypothesized that at some frequency beyond the range of their measurements a second frequency, associated with the first mode, would be found. In both gas and liquid measurements there were quantitative agreements between the measured quantities and the computed vibrational specific heats. However, Pesin and Fabelinskii[4] have measured the hyperfre-

* This research was supported by the Acoustics Branch of the U.S. Office of Naval Research.

[1] J. H. Andreae, Proc. Phys. Soc. (London) **B70**, 71–76 (1957).
[2] J. H. Andreae, P. L. Joyce, and R. J. Oliver, Proc. Phys. Soc. (London) **75**, 82–86 (1960).
[3] D. Sette, A. Busala, and J. C. Hubbard, J. Chem. Phys. **23**, 787–793 (1955).
[4] M. S. Pesin and I. L. Fabelinskii, Dokl. Akad. Nauk. SSSR **122**, 575 (1958) [English transl.: Soviet Phys.—Doklady **3**, 974 (1958)].